УДК 631.812.12:54

E. ELESHEV[1], E.KRZYWY[2], E.MOZDZER[2], Z.BAKENOVA[1]
([1]Kazakh National Agrarian University, Kazakhstan
[2]Western Pomeranian University of Technology in Szczecin, Poland)

THE EFFECT OF GRANULAR FERTILISERS PRODUCED FROM INDUSTRIAL AND MUNICIPAL WASTES ON THE CONTENT OF SOME HEAVY METALS IN TEST PLANTS

Abstrat

In the experiment being carried out, the effect of granular fertilisers being produced from industrial waste products, $CaSO_4 \cdot 2H_2O$ (waste product in production of multi-component mineral fertilisers), $FeSO_4 \cdot 7H_2O$ (waste product in production of titanium dioxide), coniferous and deciduous sawdust mixture, and municipal sewage sludge with addition of mineral fertilisers on cadmium, copper, chromium, nickel, lead and zinc contents in spring rape seeds and spring triticale grain.

The results being obtained show that the granular fertilisers being tested did not increase the content of heavy metals (Cd, Cu, Cr, Ni, Pb and Zn) in test plants above the acceptable standards. In most fertilisation objects treatments with these granular fertilisers, differences between the content of respective heavy metals in test plants were not significant. The increasing doses of granular fertilisers in most fertilisation objects did not have any significant effect on the increase in the content of heavy metals in test plants. These granular fertilisers can be used without fear of decreasing the quality of plant yields and contaminating the soil environment.

Keywords: granular fertilisers, heavy metals content in spring rape seeds and spring triticale grain

Introduction Many industrial and municipal wastes contain organic matter and plant nutrients. They can be used for fertilisation and land reclamation purposes. These wastes can also contain excessive amounts of some heavy metals and other chemical compounds and their sanitary condition may rise objections. Therefore, the wastes being intended for use in soil fertilisation and land reclamation should be subject to physical, chemical and microbiological tests. After examining the findings of these tests, a decision should be made to introduce them directly into soil or land, to subject them to technological processes to obtain fertilisers or soil improvers conforming to the standards specified in the Regulation of the Minister of Agriculture and Rural Development, or to apply another utilisation method [1-14].

The study being carried out aimed at producing four granular fertilisers from industrial waste and municipal sewage sludge and determining their effect on the content of heavy metals (cadmium, copper, chromium, nickel, lead and zinc) in spring rape seeds and spring triticale grain. These granular fertilisers were produced from calcium (II) sulphate (VI) dihydrate (being a waste product in production of titanium dioxide), iron (II) sulphate (VI) heptahydrate (being a waste product in production of multi-component mineral fertilisers), coniferous and deciduous sawdust mixture and municipal sewage sludge with addition of mineral fertilisers, ammonium phosphate, urea and 60% potassium salt.

Materials and methods To produce granular fertilisers, calcium(II) sulphate(VI) dihydrate and iron(II) sulphate(VI) heptahydrate, being waste products in the production of multi-component mineral fertilisers and titanium dioxide (as a source of sulphur), municipal sewage sludge from the Municipal Sewage Treatment Plant in Stargrad Szczeciński, and coniferous and deciduous sawdust mixture, in a 1:1 ratio, were used. The chemical analysis of the content of macroelements and some heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in respective granular fertiliser components is presented in the paper by Krzywy et al. [15]. Microbiological examinations of the sewage sludge showed that it contain no Salmonella bacteria, nor live eggs of gastrointestinal tract parasites.

Based on the chemical composition of respective components, the material composition of four fertiliser blends was formulated, calculated io dry matter. Ammonium phosphate, urea and 60% potassium salt were added to the fertiliser blends containing wastes. The addition of mineral fertilisers was intended to enable the obtained products to be included into the group of organic-mineral fertilisers and to provide the plants with optimum quantities of assimilable microelements in the first stage of development. The

produced fertiliser blends were subject to granulation, adding 2% of sodium lignosulphonate (in relation to fertiliser blend weight) as a factor facilitating this process.

The obtained granular fertilisers were subject to chemical analysis and tested in pot vegetation experiments, in which spring rape cultivar Larissa and spring triticale vcultivar Milikaro were the test plants. The pot vegetation experiment was started in 2011 for both test plants according to the same design on a soil material formed from heavy loamy sand, being counted among the rye complex of soil quality class IVb.

Two factors were taken into consideration the experiment design. The first factor was types of granular fertilisers, whereas their increasing doses (3 doses) were the second one. A single dose corresponded to 0.5 g N·pot, a doubled one to 1.0 g N·pot, while a tripled one to 1.5 g N·pot.

The cadmium, copper, nickiel, chromium and lead contents in test plants were determined by the method of atomic absorption spectrometry using a Perkin Elmer AAS 300 spectrometer. The stock solution for assays was obtained after the wet mineralisation of the plant material according to the Polish standards PN–ISO 11466 and PN-ISO 11047.

The soil material being used in the study had a slightly acidic reaction (pH 6.0). The content of plant-available phosphorus, potassium and magnesium forms was average. It amounted to 60.9, 121.0 and 42.5 $mg \cdot kg^{-1}$ D.M., respectively. The $S\text{-}SO_3$ content was low (10.2 $mg \cdot kg^{-1}$ D.M.). The total content of heavy metals in the soil material did not exceed the standards being specified in the Regulation of the Minister of Environment (table 1).

Analysis of the results of heavy metal contents in spring rape seeds and spring triticale grain was made with a two-factor analysis of variance for the randomised complete block design, using the double interaction. Confidence half-intervals were calculated for p=0.05, using the Tuckey's test.

Table 1- Material composition of fertiliser blends being subjected to granulation converted to % of dry matte

Fertiliser blend No.	% of components in fertiliser blends						
	sewage sludge	coniferous and deciduous sawdust mixture	$FeSO_4 \cdot 7H_2O$	$CaSO_4 \cdot 2H_2O$	Ammonium phosphate	Urea	KCl 60%
1	30	20	20	-	10	10	10
2	50	-	30	-	-	10	10
3	30	20	-	20	10	10	10
4	50	-	-	30	-	10	10

Table 2- Physical and chemical properties of granular fertilisers

Chemical element	Type of granular fertiliser. No in Table 1							
	1		2		3		4	
pHH_2O	5.91		6.11		5.88		6.00	
	$g \cdot kg^{-1}$d.m.	%	$g \cdot kg^{-1}$sdm.	%	$g \cdot kg^{-1}$d.m.	%	$g \cdot kg^{-1}$d.m.	%
C org.	225	22.5	220	22.0	224	22.4	222	22.2
total content								
N	7.5	7.25	66.0	6.60	74.0	7.40	65.5	6.55
P	26.0	2.60	11.0	1.00	29.0	2.80	13.6	1.36
K	50.0	5.00	50.5	5.05	50.5	5.05	51.0	5.10
Ca	7.53	0.75	22.2	1.22	55.0	5.50	84.2	8.42
Mg	0.98	0.98	1.30	0.13	1.00	0.10	1.00	0.10
S	27.0	2.70	41.0	4.10	35.0	3.50	52.2	5.22
in $mg \cdot kg^{-1}$d.m.								
$N\text{-}NH_4$	488		387		490		390	
P available	225		160		238		162	
K available	95		102		98		104	
Mg available	66		68		67		68	
total content								
Cd	0.98		1.80		0.96		1.65	
Cu	34.9		56.5		34.8		56.2	
Cr	15.8		25.9		15.9		25.8	

Ni	7.30	11.5	7.30	11.4
Pb	16.8	24.8	17.2	24.9
Zn	369	512	368	515

Results and discussion The content of heavy metals in the granular fertilisers being tested conformed to the standards for the group of organic-mineral fertilisers[7] . Due to the fact that the quality of plant yields are decided, among others, by the quantity of some heavy metals in them (Cd, Cu, Cr, Ni, Pb and Zn), in table 3 presents the harmful levels of these chemical elements in arable plants. These data will help to determine the effect of granular fertilisers on the content of heavy metals being assayed in plants.

Table 3- Harmful levels of some heavy metals in arable crops[16]. Data are given in $mg \cdot kg^{-1}$ plant D.M.

Cd	Cu	Cr	Ni	Pb	Zn
5-10	15-20	5-30	10-100	30-300	100-400

Tables 4 and 5 present the content of heavy metals in spring rape seeds, while Tables 6 and 7 show it in spring triticale grain.

The study results being obtained show that cadmium, copper, chromium, nickel, lead and zinc contents in spring rape seeds and spring triticale grain did not exceed harmful limits in any of the fertilisation objects (Tabs 3, 4, 5, 6 and 7).

The differences in cadmium, chromium, nickel and zinc contents in spring rape seeds being obtained as affected by respective granular fertilisers were not significant. Copper and lead contents in spring rape seeds were significantly higher in the fertilisation objects treatments with granular fertilisers that comprised $FeSO_4 \cdot 7H_2O$ when compared to those with calcium (II) sulphate (VI) dihydrate. The most copper was contained by spring rape seeds from the fertilisation object where the granular fertiliser comprising municipal sewage sludge (50%), $FeSO_4 \cdot 7H_2O$ (30%), urea (10%) and KCl (10%) had been applied, while the most lead from the fertilisation object 1 where the granular fertiliser comprising municipal sewage sludge (30%), sawdust (20%), $FeSO_4 \cdot 7H_2O$ (20%), ammonium phosphate (10%), urea (10%) and KCl (10%) had been applied.

The increasing doses of granular fertilisers significantly increased the lead content in spring rape seeds. The copper content in spring rape seeds from the fertilisation object treatment with a tripled dose of granular fertilisers was significantly higher when compared to a single dose. The increasing doses of granular fertilisers being tested did not have any significant effect on the increase in cadmium, chromium, nickel and zinc contents in the seeds of that test plant (Tabs 4 and 5).

The differences in the cadmium, copper and lead contents in spring triticale grain being obtained as affected by granular fertilisers were not significant. More chromium and nickel was contained by spring triticale grain in the fertilisation objects 2 and 4 where the granular fertiliser comprising 50% of municipal sewage sludge had been applied when compared to the fertilisation objects 1 and 3 where the granular fertiliser comprising 30% of municipal sewage sludge and 20% of sawdust had been applied. More zinc was contained by spring triticale grain from fertilisation objects where the granular fertilisers being applied comprised $FeSO_4 \cdot 7H_2O$ when compared to those with the granular fertilisers comprising $CaSO_4 \cdot 2H_2O$

The increasing doses of granular fertilisers did not differentiate cadmium, chromium, lead and zinc contents in spring triticale grain. As affected by the increasing doses of granular fertilisers, the copper content in the grain of that test plant significantly increased. The nickel content in spring triticale grain significantly increased in the fertilisation objects treatments with tripled doses of the granular fertilisers being tested when compared to single doses (Tabs 6 and 7).

Summing up, it is possible to conclude that the granular fertilisers being produced from industrial waste products and municipal sewage sludge did not have any effect on excessive increase in cadmium, copper, chromium, nickel, lead and zinc contents in spring rape seeds and spring triticale grain. Increase in the doses of granular fertilisers in most experimental objects treatments did not induce any significant increase in the content of heavy metals in test plants. The granular fertilisers being produced according to and presented in respect of their effect on the content of heavy metals in plants confirm the findings of studies carried out previously on the possibility of using municipal sewage sludge, calcium (II) sulphate (VI) dihydrate and iron (II) sulphate (VI) heptahydrate for fertilisation purposes [2-5,7,17-20].

Conclusions

1. Granular fertilisers did not increase the content of heavy metals (Cd, Cu, Cr, Ni, Pb and Zn) in test plants above the acceptable standards. They can be used in fertilisation of arable crops without fear. They will not have any negative effects on the quality of plant yields and the soil environment.

2. In most fertilisation objects with these granular fertilisers, differences in the content of heavy metals in test plants were not significant.

3. The increasing doses of granular fertilisers in most fertilisation objects did not have any significant effect on the increase in the content of heavy metals in test plants.

REFERENCES

1 Rozporządzenie Ministra Rolnictwa i Rozwoju Wsi z dnia 18 czerwca 2008 r. w sprawie wykonywania niektórych przepisów ustawy o nawozach i nawożeniu // DzU z dnia 2 lipca 2008 r. nr 119, poz.765. Regulation of the Minister of Environment Official Journal of Laws No. 165, item 1359 of 2002.

2 Baran S. Sludge in the economy of agri-environmental. Zesz. Prob. Post. Nauk Rol. 2004. 499:15-20.

3 Kalembasa S. Agricultural use of sewage sludge // W:substancje humusowe w glebach i nawozach. Praca zbiorowa pod redakcją Dąbskiej C i Goneta S.S., Wrocław P.T.S/H.S.:2003. 63-74.

4 Krzywy E., Wołoszyk Cz., Głowacka A. & Krzywy J. Studies on fertilizer use some industrial and municipal waste.// IV Konferencja Technologie bezodpadowe i zagospodarowanie odpadów w przemyśle chemicznym i rolnictwie. Politechnika Szczecińska. Prace,1998. 547:33-38.

5 Krzywy E. & Jakubowski W. Effect of $FeSO_4$ $7H_2O$ waste phosphogypsum and the sulfur content in the soil, iron, cadmium and nickel. Zesz. Probl. Nauk Rol 2000. 472:443-448.

6 Krzywy E., Wołoszyk C., & Iżewska A. Production and agricultural use of sewage sludge compost with the addition of the various components. Wyd. PTIE Oddział Szczeciński: 2002.39.

7 Krzywy E., Możdżer E. & Iżewska A. Research on the use of industrial wastes for the production of organic and mineral fertilizers and their impact on soil fertility. Sprawozdanie końcowe z badań przeprowadzonych w ramach projektu badawczego MNiSW NN 2012.305 155136, ss. 70.

8 Krzywy J.Measure residual sulfate (VI) iron (II) to yield a mixture of grasses, and on the enzymatic activity of the soil. Uniwersytet Warmińsko-Mazurski w Olsztynie. Praca doktorska, 2001. ss. 86.

9 Pasikowski K. Studies on the use of 7 hydrate (VI) iron (II) for use as fertilizers. Praca doktorska. Akademia Rolnicza w Szczecinie 2000. ss. 86.

10 Rosik-Dulewska C. Basics of Waste Management. Wyd. PWN Warszawa. 2008.

11 Siuta J. & Wasiak G. Rules for the use of sewage sludge on non-industrial purposes (nature). Wyd. PTIE Warszawa 2001. nr 3:13-42.

12 Krzywy-Gawrońska E. The effect of industrial wastes and municipal sewage sludge compost on the quality of virginia fanpetals (SIDA HERMAPHRODITA RUSBY) biomass. Part 1. Macroelements content and their upatke dynamics. Polish Journal of Chemical Technology.2012. 14(2):9-15.

13 Krzywy-Gawrońska E., The effect of industrial wastes and municipal sewage sludge compost on the quality of virginia fanpetals (SIDA HERMAPHRODITA RUSBY) biomass. Part 2. Heavy metals content, their uptake dynamics and bioaccumulation. Polish Journal of Chemical Technology 2012. 14(3):8-14.

14 Krzywy E, Możdżer E. & Bekanowa Ż. The effect of granular fertilisers produced from industrial and municipal wastes on the crop yield and their content of macroelements Polish Journal of Chemical Technology. Praca zarejstrowana pod nr KBO 2013.8/2013

15 Krzywy E, Możdżer E., Iżewska A. & Jałoszyński S. The possibility of producing granular fertilisers from municipal sewage sludge and industrial waste. Przemysł Chemiczny 2013.92(4):531-534.

16 Kabata-Pendias A. & Pendias H., Biogeochemistry of trace elements. Wyd. PWN Warszawa 1999.ss.400.

17 Krzywy E., Wołoszyk C., & Iżewska A. The value of municipal sewage sludge fertilizer. Wyd. PTIE Oddział Szczeciński: 2000. 58.

18 Rozmarynowska M. Research on the effects of foliar sulfur and iron by-product of $FeSO_4 \cdot 7H_2O$ on the quantity and quality characteristics of crop plants. Praca doktorska. Zachodniopomorski Uniwersytet Technologiczny w Szczecinie 2009. ss. 119.

19 Krzywy E., Krzywy J., & Krzywy-Gawrońska E. The influence of foliar fertilization by water solution of 7 hydrate sulphate (VI) iron (II) on yielding and chemical composition of cropsi. I. The influence of foliar fertilization with water solution of 7 hydrate sulphate (VI) iron (II) on crops yield quantity. Polish Journal of Chemical Technology 2005. 7:16-18.

20 Krzywy E., Krzywy J. & Krzywy-Gawrońska E. The influence of foliar fertilization by water solution of 7 hydrate sulphate (VI) iron (II) on yielding and chemical composition of cropsi. II. The influence of foliar fertilization with water solution of 7 hydrate sulphate (VI) iron (II) on content of nitrogen, phosphorus, potassium, calcium, magnesium, sulphur and iron in plants. Polish Journal of Chemical Technology 2005. 7:19-21.

E.Eleshev, E.Krzywy, E.Mozdzer, Z.Bakenova

THE EFFECT OF GRANULAR FERTILISERS PRODUCED FROM INDUSTRIAL AND MUNICIPAL WASTES ON THE CONTENT OF SOME HEAVY METALS IN TEST PLANTS

Е.Елешев, Э.Кшивы, Э.Модзер, Ж.Бакенова

ВЛИЯНИЕ ГРАНУЛИРОВАННЫХ УДОБРЕНИЙ ПРОИЗВОДИМЫХ ИЗ ИНДУСТРИАЛЬНЫХ И МУНИЦИПАЛЬНЫХ ОТХОДОВ НА СОДЕРЖАНИЕ НЕКОТОРЫХ ТЯЖЕЛЫХ МЕТАЛЛОВ

Е.Елешев, Э.Кшивы, Э.Модзер, Ж.Бакенова

ИНДУСТРИАЛДЫ ЖӘНЕ МУНИЦИПАЛДЫ ҚАЛДЫҚТАРДАН ӨНДІРІЛГЕН ТҮЙІРШІКТЕЛГЕН ТЫҢАЙТҚЫШТАРДЫҢ КЕЙБІР АУЫР МЕТАЛДАРДЫҢ МӨЛШЕРІНЕ ӘСЕРІ

Резюме

Орындалған эксперименттік жұмыста өндірістік қалдықтардан өндірілген түйіршіктелген тыңайтқыштардағы, $CaSO_4 \cdot 2H_2O$, $FeSO_4 \cdot 7H_2O$, қылқан жапырақты және жапырақты ұнтақ араласпаларындағы муниципалды ағын суларға қосқан минералдық тыңайтқыштардың құрамдарындағы кадмийдің, мыстың, хромның, никельдің, қорғасынның және цинктің мөлшерін анықтау зерттелген.

Тәжірибе мәліметтері бойынша, тексеруші түйіршіктелген тыңайтқыштар сыналып жатқан зауыттарда ауыр металдардың мөлшерін тиімді стандарттан жоғары көтермеді.

Бұл түйіршіктелген тыңайтқыштар ауылшаруашылығы өнімі сапасын және қоршаған ортаны (топырақты) ластамайды.

Резюме

В выполняемом эксперименте изучается содержание кадмия, меди , хрома, никеля, свинца и цинка в гранулированных удобрениях, производимых из продуктов промышленных отходов, $CaSO_4 \cdot 2H_2O$, $FeSO_4 \cdot 7H_2O$, хвойных и лиственных смесях опилок, муниципальных отстоях вод с добавлением минеральных удобрений.

По результатам опыта, гранулированные проверяемые удобрения не увеличивали содержание тяжелых металлов (Cd, Cu, Cr, Ni, Pb and Zn) на испытательных заводах выше приемлемых стандартов. Эти гранулированные удобрения могут использоваться без страха уменьшением качества урожаев и загрязнения среды почвы.

Сведения об авторах

Рахимжан Елешев
1. д.с.-х.н., профессор, академик НАН РК и РАСХН
2. Казахстан, г.Алматы, пр.Абая 8
3. Казахский национальный аграрный университет

Эдвард Кшивы
1. д.с.х.н., профессор
2. Польша, г. Щецин, ул Словацкого 17
3. Западно-Поморский Технологический университет

Ева Модзер
1. к.с.-х.н., доцент
2. Польша, г. Щецин, ул Словацкого 17
3. Западно-Поморский Технологический университет

Женисгуль Бакенова
1. доктор PhD
2. Казахстан, г.Алматы, пр.Абая 8
3. Казахский национальный аграрный университет